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Sustainable hydrogen production from steam reforming of bio-oil model compound based on carbon deposition/elimination

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ABSTRACT

Steam reforming of crude bio-oil or some heavy component present in bio-oil is a great challenge for sustainable hydrogen production due to the extensive coke formation and catalyst deactivation. Catalyst regeneration will be an unavoidable operation in this process. In this paper, m-cresol (a model compound derived from bio-oil) was steam reformed on commercial Ni-based catalyst. Two conventional carbon elimination methods for coked catalyst were applied and the results showed that sustainable hydrogen production can be obtained based on carbon deposition/elimination. The carbon deposition can be gasified easily under certain temperature. The activity of regenerated catalyst samples can be nearly recovered as the fresh ones. Under the reaction conditions of 850 °C and steam to carbon ratio 5:1, >66% hydrogen mole fraction, >81% hydrogen yield, and >97% carbon conversion can be achieved based on regenerated catalyst. Catalyst characterization indicated that the loss of active metal can be considered as the main reason for tiny activity drop. Ni redispersion and Fe contamination may be another two factors that influence catalyst activity.

1. Introduction

In recent years, biomass energy as a kind of clean energy has attracted great attention in the world. Biomass can be gasified easily to generate syngas or fuel gas [1–3]. Through hydrolysis and fermentation technologies, biomass such as lignocellulose can be converted to fuel ethanol [4–6]. Through pyrolysis technologies [7–9], biomass can be converted to bio-oil. Biomass pyrolysis technologies such as flash pyrolysis [10], vacuum pyrolysis [11], microwave pyrolysis [12], rotating cone pyrolysis [13] and vortex pyrolysis [14] developed rapidly in recent years. Under the proper reaction conditions, bio-oil yield can reach as high as 80%. But in current stage, due to the bad properties of bio-oil, such as high oxygen content, low heat value, and high corrosivity, it's a great challenge for bio-oil to be used as engine fuel. Therefore, how to use the bio-oil properly and effectively has attracted researchers' great attention in the world. Bio-oil/diesel emulsion for engine fuel [15,16], bio-oil upgrading by catalytic cracking [17], hydrotreatment [18] and esterification [19], bio-oil separation for valuable chemicals [20–22], bio-oil gasification for syngas [23], and bio-oil steam reforming for hydrogen production [24,25] are the main technological routes that researchers studied in recent years. In the presence of catalyst, H_2-rich gas can be generated through bio-oil steam reforming and the hydrogen composition can reach as high as 50%–60%. Compared to hydrogen production from biomass, it has two obvious advantages: on one hand, bio-oil has much higher energy

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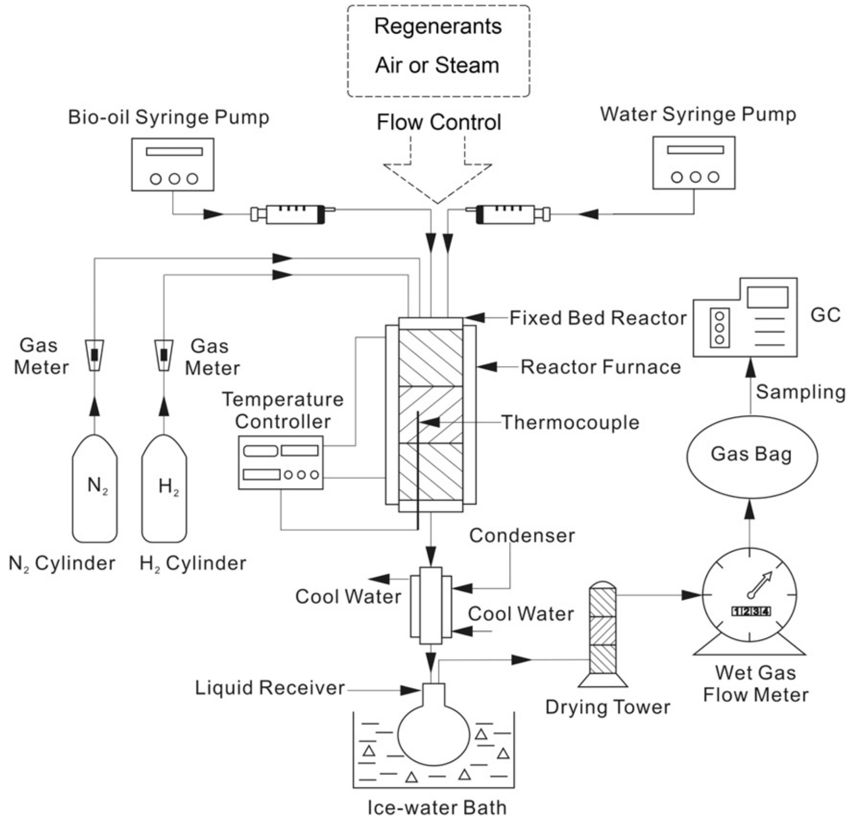

Fig. 1 – Schematic diagram of experimental apparatus for catalytic steam reforming of bio-oil and catalyst regeneration.

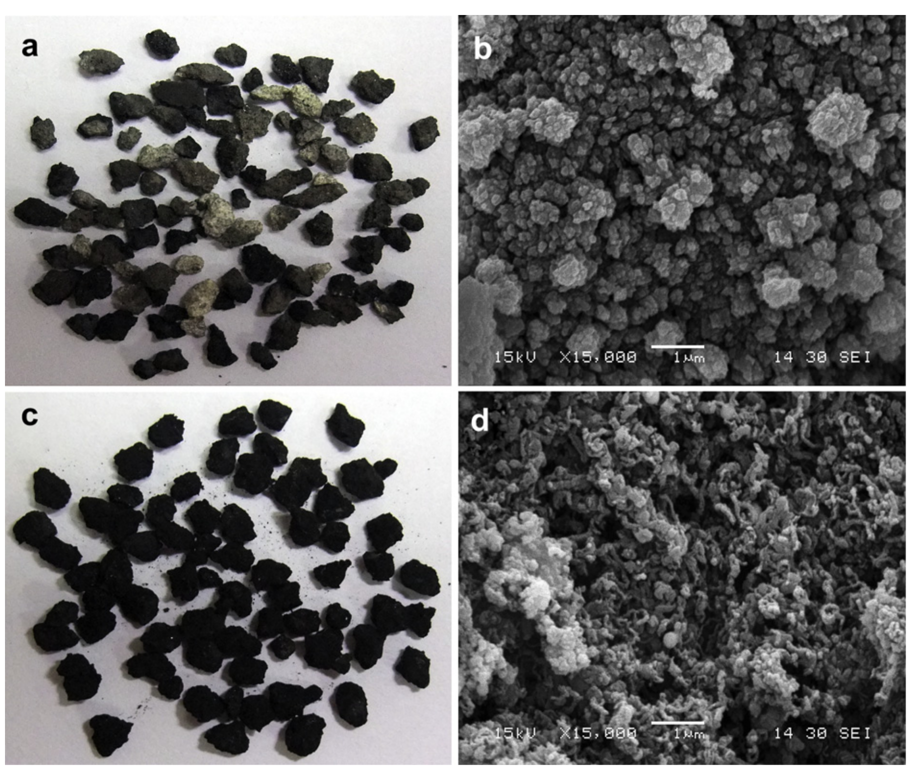

Fig. 2 – External appearances and SEM images of fresh (a, b) and coked (c, d) catalyst samples.

density than that for biomass. It can be collected from scattered pyrolysis plants faraway and then transported to steam reforming plants to produce hydrogen intensively. In this process, the transportation costs can be reduced effectively. On the other hand, for the liquid state of bio-oil, the complicated feeding system can be avoided. Simple liquid pump can be qualified for the feeding work. In recent years, many researchers in the world have started the research on steam reforming of bio-oil. D. Wang et al. [26,27] in NREL investigated the chemical and economic feasibilities of bio-crude steam reforming in 1990s. They pointed out that bio-oil or its aqueous fraction can be efficiently reformed to generate hydrogen by a thermocatalytic process using commercial, Ni-based catalysts. At the same time, researchers have done a lot of work focusing on catalyst preparation and modification [28–34] to improve the catalyst performance especially for carbon deposition resistance.

Our previous work has proved that heavy bio-oil components can form carbon on catalyst much more easily than that for light fractions [35]. In order to solve the severe problems caused by coke formation, we have tested a two-stage reactor system [25]. At the same time, a detailed study on carbon deposition behaviors has been studied in literature [36]. Generally, for a long reaction duration, steam reforming of bio-crude or some heavy component present in bio-oil is difficult due to extensive coke formation and catalyst deactivation. It will also cause some operation problems such as reactor tube blockage and pressure rising. Naturally, carbon elimination and catalyst regeneration will be an unavoidable work in steam reforming of bio-oil for sustainable hydrogen production.

In this work, a heavy bio-oil model compound m-cresol was steam reformed on a high-efficient Ni-based catalyst. In this process, the coked catalyst samples can be obtained. Two conventional carbon elimination methods including combustion method and steam gasification method were applied to achieve the catalyst regeneration. Through different characterization methods, catalyst activity, composition and structure changes were investigated. Based on carbon deposition/elimination, sustainable hydrogen production from steam reforming of bio-oil model compound was evaluated. The detailed carbon deposition behaviors have been studied in our previous work [36]. This paper can be regarded as an extended study of this kind of research.

2. Experimental

2.1. *Flow sheet, materials, and analytical methods*

Catalytic steam reforming of bio-oil model compound was carried out based on a set of fixed bed reactor system. The schematic diagram of experimental apparatus can be shown as Fig. 1. The detailed operation procedure can be found in literature [36]. When steam reforming work was completed and reactor temperature dropped to ambient value, a catalyst regeneration procedure will be carried out. In this paper, two regenerants (air and steam) were used to eliminate the carbon deposition. The flow rate of air or steam can be controlled by gas pump and gas flow meter.

Phenols are very common heavy components present in crude bio-oil. In our previous work [25], their proportion in fast pyrolysis bio-oil can reach as high as 13% with sawdust as pyrolysis material. In addition, it has been proved that phenols can form carbon deposition easily in steam reforming process [35,36]. In this paper, a heavy bio-oil model compound pure m-cresol (C_7H_8O) was chosen for the test to ensure the investigation is valuable and forceful. For the merits of low costs and high selectivity for hydrogen, a high-efficient commercial Ni-based catalyst was used in the experiment. The pure m-cresol was provided by Sinopharm Chemical Reagent Co., Ltd., China. Ni/MgO (YWC series) was provided by Wuxi Qiangya Co. Ltd., China. The catalyst composition is MgO>80%, Al_2O_3>6%, Ni>6%, and rare-earth element<0.5%. The specific surface area is 1–3 m^2/g. The catalyst was crushed and the grains in particle size range of 0.9–1.1 mm were sieved out for the test.

Via different analytical methods, gas composition, carbon deposition behaviors and catalyst characteristics can be determined, respectively. The detailed data analysis and calculation methods can be found in literature [36].

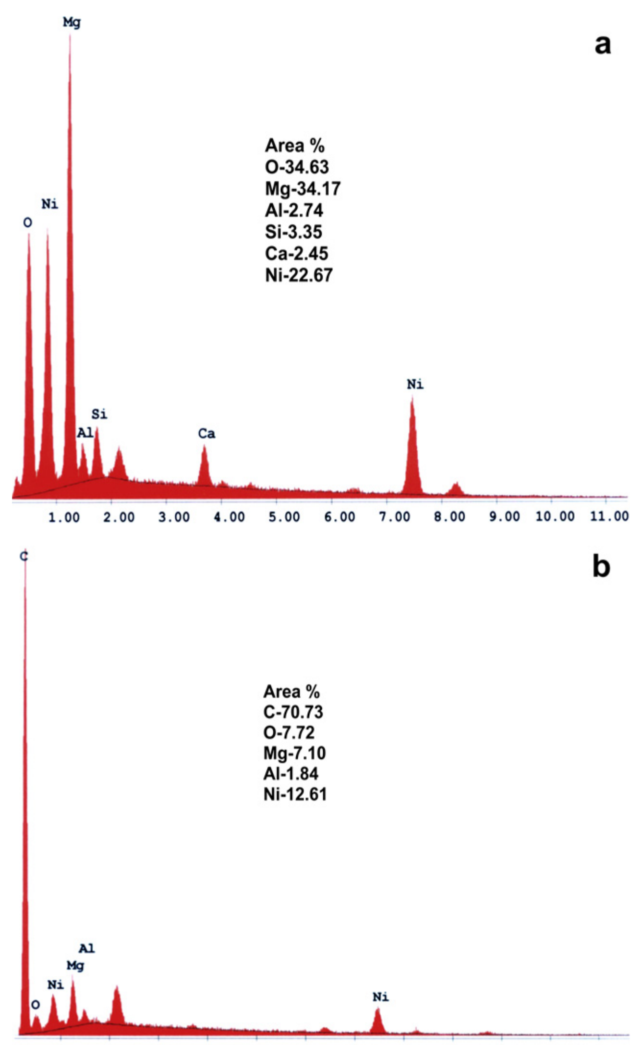

Fig. 3 – EDS patterns of fresh (a) and coked (b) catalyst samples.

3. Results and discussion

3.1. *Preparation and characterization of coked catalyst samples*

In this part, the coked catalyst samples were prepared under the reaction conditions of m-cresol feeding rate 10.0 g/h, steam to carbon ratio (S/C) 5:1, catalyst loading content 10.0 g, and reaction temperature 850 °C. The detailed carbon deposition behaviors studied in literature [36] indicated that m-cresol is a compound which can form carbon deposition easily on catalyst even under higher reaction temperature (800–900 °C). For a long reaction time, the carbon deposition can grow gradually in form of carbon nanofiber and the reactor tube finally can be blocked. In this part, m-cresol was steam reformed in 3 h reaction time. When reactor temperature dropped to ambient value, the coked catalyst sample was collected and characterized by the methods of SEM, EDS and XRD, respectively. Fig. 2 shows the external appearances and SEM images of fresh as well as coked catalyst samples. The EDS and XRD results can be shown as Fig. 3 and Fig. 4, respectively.

From Fig. 2-a, the external appearance of fresh catalyst sample is in dark grey. And the SEM image Fig. 2-b shows that it has a very rough surface structure. Compared to the fresh sample, Fig. 2-c shows a very different external appearance in color and surface roughness. It is obvious that the catalyst surface has been blocked by carbon coating. The SEM image of coked catalyst sample in Fig. 2-d indicates that the catalyst surface has been blocked by extensive carbon nanofiber. The carbon content of coked catalyst was determined by TG method. The coked catalyst was grounded to powder and a 30 mg sample was placed in the analyzer and the sample was first heated to 100 °C under argon to outgas water. Then a temperature ramp (15 °C/min, from 100 to 800 °C) was applied under a 20% O_2/Ar (100 mL/min) flow. TG result shows that the carbon content of coked catalyst sample is 7.9 wt.%. Literature [37] obtained as high as 12 wt.% carbon content in steam reforming of crude bio-oil using noble metal catalyst. It is obvious that the carbon deposition is very severe using bio-oil or its heavy model compound as feeding material. An operation aiming at carbon elimination and catalyst regeneration should be carried out.

Fig. 3 shows the EDS patterns of fresh and coked catalyst samples. Catalyst elementary composition can be seen in Fig. 3-a. The main body of Ni-based catalyst is consisted of O, Ni, Mg, Al, Si and Ca. But in Fig. 3-b, an obvious carbon peak nearly override the other element peaks. For the extensive carbon blockage, Si and Ca elements can no longer be discerned. Generally, carbon deposition can block the active center and cause catalyst deactivation. Fig. 3-b indicates that the reaction efficiency can be reduced due to the large area of

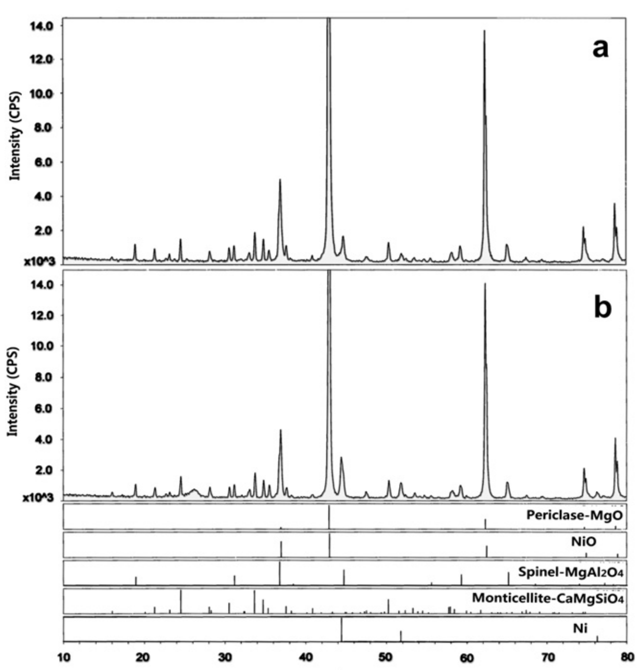

Fig. 4 – XRD patterns of fresh (a) and coked (b) catalyst samples.

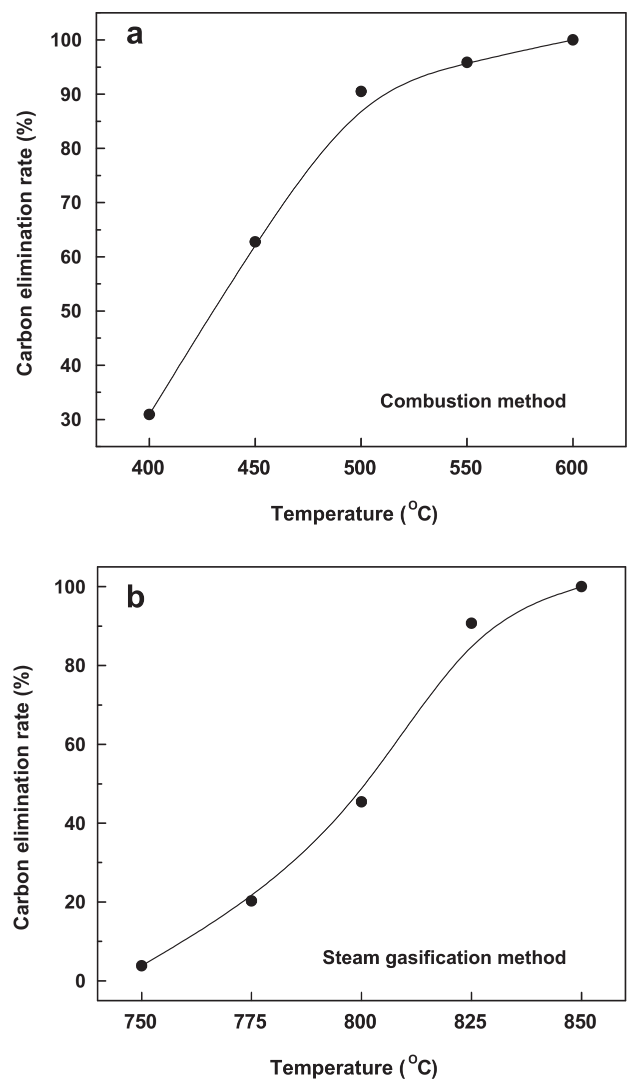

Fig. 5 – Effect of temperature on carbon elimination rate-(a), combustion method; (b), steam gasification method.

carbon deposition on catalyst surface. The data relating to catalyst deactivation can be found in literature [35]. Catalyst deactivation can cause the decrease of hydrogen yield. CH_4 and CO contents will increase.

In order to know the dispersion state of different elements in catalyst, XRD detection was done and the results can be shown as Fig. 4. From Fig. 4-a, the crystal structure of fresh catalyst can be in the form of periclase-MgO, NiO, spinel-$MgAl_2O_4$, and monticellite-$CaMgOSiO_4$. There was no Ni characteristic peak detected in the pattern. It is indicated that Ni element dispersed well on the support and its crystal structure was too tiny to detect out. But the XRD pattern of coked catalyst sample showed the obvious characteristic peaks of Ni. It can be deduced that, with the proceeding of steam reforming and carbon deposition, the active metal broke away from the catalyst surface. Ni redispersion and recrystallization occurred. Literature [38] described the detailed process of carbon formation on Ni-based catalyst. When carbon deposition occurred, the hydrocarbon can be adsorbed on catalyst surface and decomposed to carbon atom and carbonaceous atomic groups. They will stay on catalyst surface and block metal atoms. With the growth of carbide, Ni particle was forced to break away from the catalyst main body. Finally, a carbide pillar can be formed. The catalyst active center and micropore can be blocked by these carbide pillars. Finally, catalyst was deactivated. Catalyst deactivation will cause the decrease of bio-oil conversion and the increase of methane content. In addition, hot spot phenomenon will appear and the service life of furnace tube will be reduced. Compared with the fresh catalyst sample (Fig. 3-a), the relative ratio of Ni to the other elements (expect for carbon) in Fig. 3-b became much higher. It can be deduced that certain content of Ni had been separated from catalyst main body and dissolved in carbon pillars. This result is in agreement with the description in literature [38].

3.2. *Carbon elimination and catalyst regeneration*

As mentioned above, catalyst deactivation and some operation problems will be caused with the accumulation of carbon deposition. In this part, an operation aiming at carbon elimination and catalyst regeneration was carried out. Two conventional carbon elimination methods including combustion method and steam gasification method were applied. The reactions about combustion method and steam gasification method can be shown as Eq. (1) and Eq. (2), respectively.

$$C + O_2 \rightarrow CO_2 \quad (1)$$

$$C + 2H_2O \rightarrow 2H_2 + CO_2 \quad (2)$$

For both of the carbon elimination methods, to ensure that the reaction can undergo completely, carbon elimination was carried out under the conditions of gas (air or steam) flow rate 300 mL/min and reaction time 2 h. This means if the reaction temperature is proper, theoretical 100% carbon elimination rate can be achieved. The carbon elimination operation was still based on the fixed bed reactor system.

Fig. 5 shows the results of effect of temperature on carbon elimination rate: a, combustion method; b, steam gasification

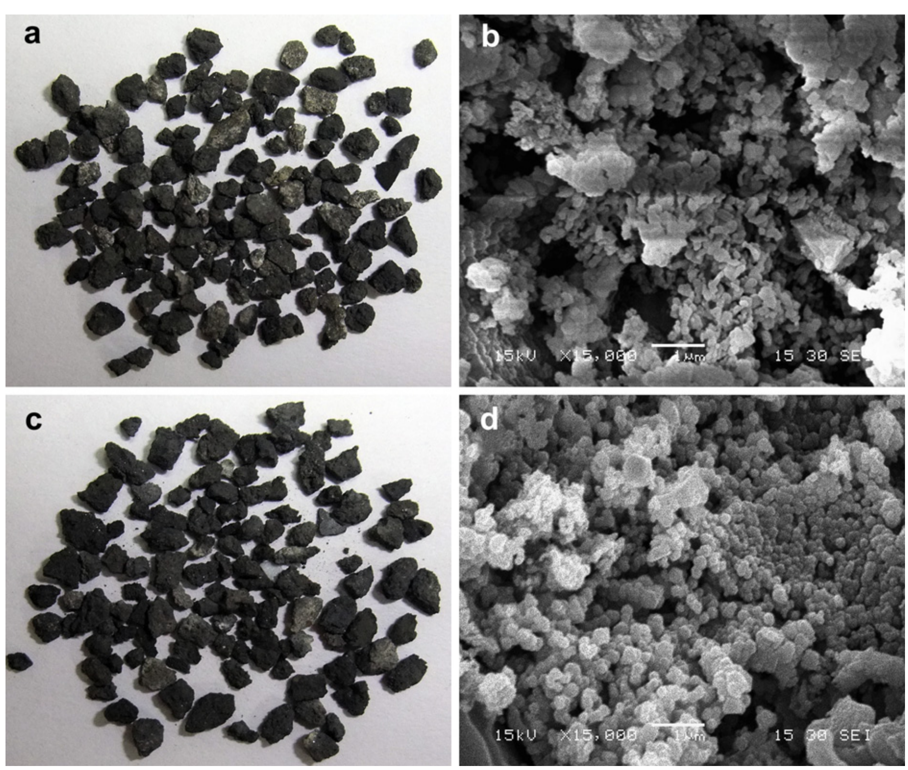

Fig. 6 – External appearances and SEM images of regenerated catalyst samples-(a, b), obtained by combustion method; (c, d), obtained by steam gasification method.

method. The carbon elimination rate can be defined as the ratio of eliminated carbon to total carbon deposition. From the results shown in Fig. 5-a and Fig. 5-b, there is significant difference between the two methods. For combustion method, the carbon can be eliminated obviously in temperature range 400–600 °C. 600 °C was high enough to eliminate the carbon deposition completely. For steam gasification method, much higher temperature was required. Obvious carbon elimination occurred in temperature range 750–850 °C. 100% carbon elimination rate can be obtained at high temperature point of 850 °C. Alenazey et al. [39] used O_2, air, CO_2, H_2 and N_2 as gasifying agents to remove the coke. They pointed out that carbon removal mechanism is dependent on the gasifying agent. Carbon removal under different gasifying agents will follow the different reaction models. In our work of this paper, for the two carbon elimination methods, carbon combustion can work under relatively lower temperature. This may be a better choice in view of energy consumption. But as a by-product, the carbon deposition was only treated as a kind of reaction wastes. For coke steam gasification, although the temperature required was higher, the carbon deposition was used as a new material to generate hydrogen. In view of energy consumption and by-product recycling, further evaluation on these two methods should be investigated in the future research work. But it is important to mention that, the reaction temperature range is acceptable for such a severe carbon deposition state. Perfect carbon elimination can be achieved by both of the methods.

Fig. 6 shows the external appearance and SEM image of regenerated catalyst samples. Through the two regeneration methods, the catalyst particles can be recovered to the normal color and the clear surface structure appeared again. In order to know the elementary composition changes before and after regeneration, EDS analysis was also done. Fig. 7 shows the EDS patterns for the regenerated catalyst samples. Compared to the fresh catalyst sample, Ni content shows an obvious drop for both of the samples. It is proved again that Ni broke away from catalyst main body due to the growth of carbon fiber. Another important change was observed that a new element Fe was detected in the pattern. There is no Fe element contained in catalyst itself. It can be deduced that the Fe element is a contaminant coming from outside. In steam reforming process, the hydrothermal reactions caused the corrosion of reactor inner tube. Tiny content of Fe element broke away from the stainless steel tube and finally fell to catalyst main body. Fig. 8 shows the XRD patterns of regenerated catalyst samples. For combustion method, the crystal structure for regenerated catalyst sample can be in the form of periclase-MgO, NiO, spinel-$MgAl_2O_4$, and monticellite-$CaMgOSiO_4$. For steam gasification method, Ni characteristic peaks can be detected in the pattern. It is obvious that Ni dispersion state on support changed with the proceeding of carbon deposition/carbon elimination reactions.

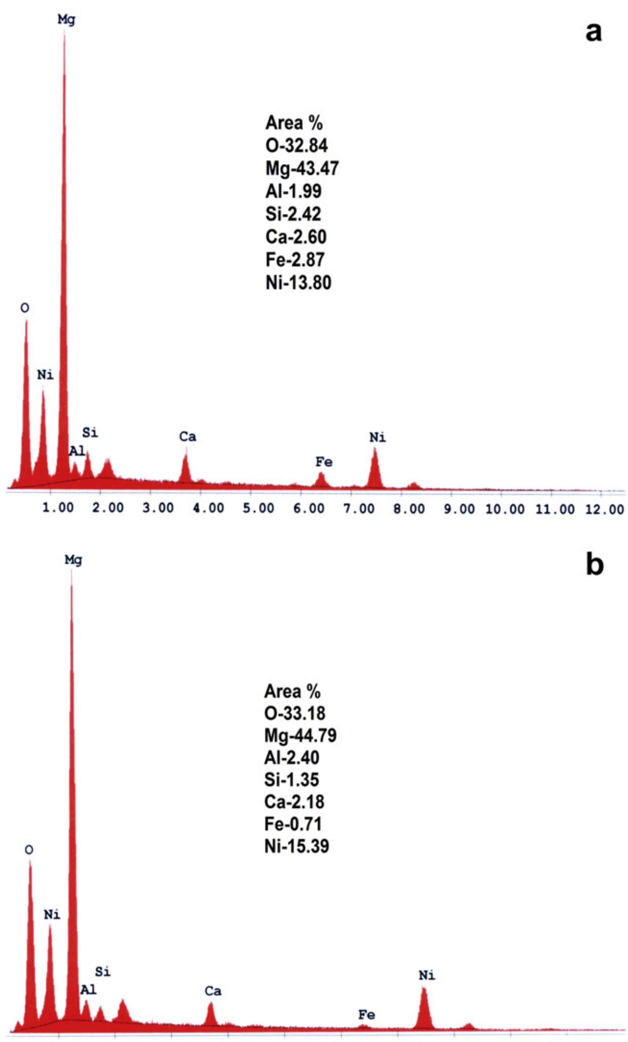

Fig. 7 – EDS patterns of regenerated catalyst samples-(a), obtained by combustion method; (b), obtained by steam gasification method.

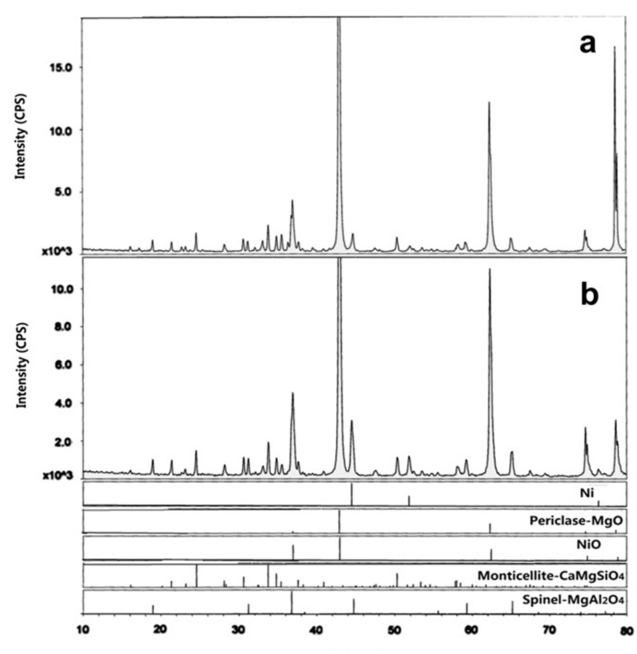

Fig. 8 – XRD patterns of regenerated catalyst samples-(a), obtained by combustion method; (b), obtained by steam gasification method.

3.3. *Activity test of regenerated catalysts*

In this part, m-cresol was steam reformed on regenerated catalyst samples to elucidate the activity changes. The data of steam reforming on fresh catalyst was also provided. The reaction conditions were kept the same as what mentioned in 3.1. The results about gas composition, hydrogen yield and gaseous carbon conversion can be shown as Fig. 9 and Fig. 10.

From Fig. 9, it can be seen that high hydrogen compositions (66–68%) can be obtained by the three reactions. At the same time, CH_4 compositions were kept at very low levels (0.2–0.5%). From an industrial point of view, CO can be converted to H_2 very easily (see Eq. (3)) and the desirable gas production purity can reach more than 99%. For regenerated catalyst samples, they showed tiny drops in H_2 mole fraction. Mole fractions of CO and CH_4 showed little increases. From hydrogen yield shown in Fig. 10-a, catalyst activity dropped tinily after regeneration. For combustion method, hydrogen yield dropped from 84.0% to 81.3%, and for steam gasification method, it dropped to 82.9%. Fig. 10-b illustrates the carbon conversion before and after catalyst regeneration. It shows a similar result to that for hydrogen yield. From the results above, it can be deduced that active metal loss is the main reason for catalyst activity drop. Ni redispersion and Fe contamination may be another two inhibited factors to catalyst activity. It is important to mention that, although the activity of regenerated catalyst showed little drops, the overall level was still kept at high values. Based on regenerated catalysts, >66% hydrogen mole fraction, >81% hydrogen yield, and >97% carbon conversion can still be achieved.

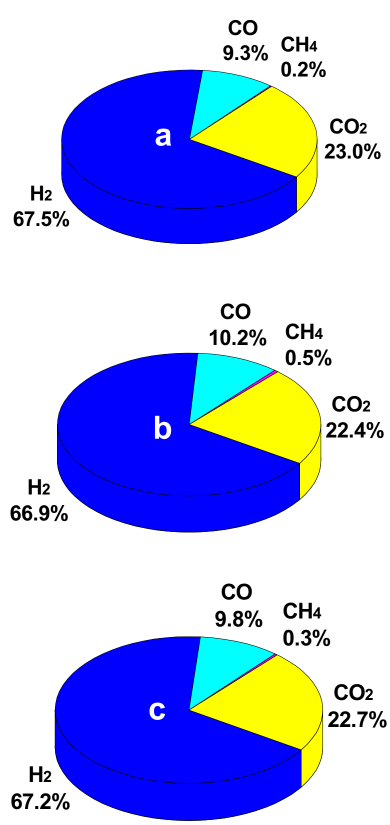

Fig. 9 – Gas product mole fractions obtained by fresh catalyst (a), catalyst regenerated by combustion method (b), and catalyst regenerated by steam gasification method (c).

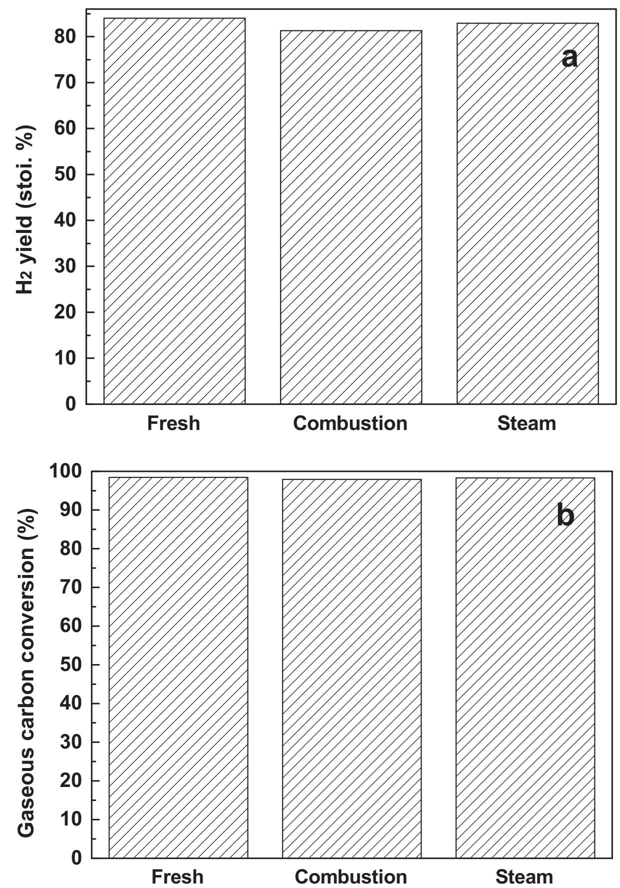

Fig. 10 – H_2 yield (a) and gaseous carbon conversion (b) obtained by fresh catalyst, catalyst regenerated by combustion method, and catalyst regenerated by steam gasification method.

$$CO + H_2O \rightarrow H_2 + CO_2 \tag{3}$$

Carbon elimination and catalyst regeneration will be an unavoidable operation in steam reforming of bio-crude or some heavy components present in bio-oil. The results obtained in this paper prove that carbon deposition can be eliminated easily using simple facilities and methods. Of course, some catalyst properties will be degraded with the proceeding of carbon deposition/elimination. With the rapid development of catalyst preparation technologies, more high-efficient catalysts will be developed. Some researchers have studied the effects of catalyst composition [40] and some have developed the new type noble metal catalysts [33,41–43]. In order to reduce the carbon deposition, some researchers have tried to design the fluidized bed reactor and input certain content of oxygen in reaction system [44]. But in current stage, it's still a great challenge to carry out the bio-crude steam reforming in long time duration due to the extensive coke formation and catalyst deactivation. In this paper, coke formation indeed made a big problem in steam reforming of m-cresol, a model compound derived from bio-oil. For such

a severe carbon deposition state, carbon deposition/elimination procedure can provide an alterative route for sustainable hydrogen production.

4. Conclusions

Extensive coke formation and catalyst deactivation can be caused in steam reforming of bio-oil or some heavy components present in bio-oil. In this paper, coked catalyst samples were prepared in steam reforming of m-cresol, a heavy model compound derived from bio-oil. Severe coke formation on Ni-based catalyst made it necessary to carry out the procedure of carbon elimination. Two carbon elimination methods (combustion method and steam gasification method) were applied. For combustion method, carbon deposition can be eliminated easily under 600 °C. For steam gasification method, higher temperature point 850 °C was required to achieve 100% carbon elimination rate. The activity of regenerated catalyst samples showed tiny drops, which can be mainly due to the loss of active metal. Ni redispersion and Fe contamination could be another two inhibited factors. Under the conditions of 850 °C and steam to carbon ratio 5:1, >66% hydrogen mole fraction, >81% hydrogen yield, and >97% carbon conversion can still be achieved based on regenerated catalysts. It provided an alternative route to generate sustainable hydrogen based on carbon deposition/elimination.

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REFERENCES

[1] Miles TR, Miles Jr TR. Overview of biomass gasification in the USA. Biomass 1989;18:163–8.
[2] Acharya B, Dutta A, Basu P. An investigation into steam gasification of biomass for hydrogen enriched gas production in presence of CaO. International Journal of Hydrogen Energy 2010;35:1582–9.
[3] Lv P, Yuan Z, Wu C, Ma L, Chen Y, Tsubaki N. Bio-syngas production from biomass catalytic gasification. Energy Conversion and Management 2007;48:1132–9.
[4] Sun Y, Cheng J. Hydrolysis of lignocellulosic materials for ethanol production: a review. Bioresource Technology 2002; 83:1–11.
[5] Ladisch MR, Svarczkopf JA. Ethanol production and the cost of fermentable sugars from biomass. Bioresource Technology 1991;36:83–95.
[6] Brethauer S, Wyman CE. Review: continuous hydrolysis and fermentation for cellulosic ethanol production. Bioresource Technology 2010;101:4862–74.
[7] Lédé J, Broust F, Ndiaye FT, Ferrer M. Properties of bio-oils produced by biomass fast pyrolysis in a cyclone reactor. Fuel 2007;86:1800–10.
[8] Zheng J. Bio-oil from fast pyrolysis of rice husk: yields and related properties and improvement of the pyrolysis system. Journal of Analytical and Applied Pyrolysis 2007;80:30–5.
[9] Ate F, Pütün E, Pütün AE. Fast pyrolysis of sesame stalk: yields and structural analysis of bio-oil. Journal of Analytical and Applied Pyrolysis 2004;71:779–90.
[10] Scott DS, Piskorz J. The flash pyrolysis of aspen-poplar wood. The Canadian Journal of Chemical Engineering 1982;60: 666–74.
[11] Pakdel H, Roy C. Chemical characterization of wood oils obtained in a vacuum pyrolysis process development unit. ACS Preprints (Div. Fuel Chem.) 1987;32(2):203–14.
[12] Krieger-Bockett B. Microwave pyrolysis of biomass. Research on Chemical Intermediates 1994;20(1):39–49.
[13] Wagenaar BM, Prins W, Vanswaaij WPM. Pyrolysis of biomass in the rotating cone reactor: modeling and experimental justification. Chemical Engineering Science 1994;49(24):5109–26.
[14] Diebold J, Scahill J. Production of primary oils in a vortex reactor. ACS Preprints (Div. Fuel Chem.) 1987;32(2):21–8.
[15] Chiaramonti D, Bonini M, Fratini E, Tondi G, Gartner K, Bridgwater AV, et al. Development of emulsions from biomass pyrolysis liquid and diesel and their use in engines-Part 1: emulsion production. Biomass and Bioenergy 2003;25:85–99.
[16] Chiaramonti D, Bonini M, Fratini E, Tondi G, Gartner K, Bridgwater AV, et al. Development of emulsions from biomass pyrolysis liquid and diesel and their use in engines-Part 2: tests in diesel engines. Biomass and Bioenergy 2003; 25:101–11.
[17] Sharma RK, Bakhshi NN. Conversion of non-phenolic fraction of Biomass-Derived pyrolysis oil to hydrocarbon fuels over HZSM-5 using a dual reaction system. Bioresource Technology 1993;45:195–203.
[18] Fisk CA, Morgan T, Ji Y, Crocker M, Crofcheck C, Lewis SA. Bio-oil upgrading over platinum catalysts using in situ generated hydrogen. Applied Catalysis A: General 2009;358 (2):150–6.
[19] Miao S, Shanks BH. Esterification of biomass pyrolysis model acids over sulfonic acid-functionalized mesoporous silicas. Applied Catalysis A: General 2009;359(1–2):113–20.
[20] Wang S, Gu Y, Liu Q, Yao Y, Guo Z, Luo Z, et al. Separation of bio-oil by molecular distillation. Fuel Processing Technology 2009;90(5):738–45.
[21] Murwanashyaka JN, Pakdel H, Roy C. Separation of syringol from birth wood-derived vacuum pyrolysis oil. Separation and Purification Technology 2001;24:155–65.
[22] Chen CA, Pakdel H, Roy C. Separation of phenols from eucalyptus wood tar. Biomass and Bioenergy 1997;13(1–2): 25–37.
[23] Panigrahi S, Dalai AK, Chaudhari ST, Bakhshi NN. Synthesis gas production from steam gasification of biomass-derived oil. Energy & Fuels 2003;17:637–42.
[24] Davidian T, Guihaume N, Iojoiu E, Provendier H, Mirodatos C. Hydrogen production from crude pyrolysis oil by a sequential catalytic process. Applied Catalysis B: Environmental 2007; 73:116–27.
[25] Wu C, Huang Q, Sui M, Yan Y, Wang F. Hydrogen production via catalytic steam reforming of fast pyrolysis bio-oil in a two-stage fixed bed reactor system. Fuel Processing Technology 2008;89(12):1306–16.
[26] Wang D, Montané D, Chornet E. Catalytic steam reforming of biomass-derived oxygenates: acetic acid and hydroxyacetaldehyde. Applied Catalysis A 1996;143:245–70.
[27] Wang D, Czernik S, Chornet E. Production of hydrogen from biomass by catalytic steam reforming of fast pyrolysis oils. Energy & Fuels 1998;12:19–24.
[28] Hou T, Yuan L, Ye T, Gong L, Tu J, Yamamoto M, et al. Hydrogen production by low-temperature reforming of

organic compounds in bio-oil over a CNT-promoting Ni catalyst. International Journal of Hydrogen Energy 2009;34: 9095–107.

[29] Muroyama H, Nakase R, Matsui T, Eguchi K. Ethanol steam reforming over Ni-based spinel oxide. International Journal of Hydrogen Energy 2010;35:1575–81.

[30] Liu S, Chen D, Zhang K, Li J, Zhao N. Production of hydrogen by ethanol steam reforming over catalysts from reverse microemulsion-derived nanocompounds. International Journal of Hydrogen Energy 2008;33:3736–47.

[31] Liu JY, Lee CC, Wang CH, Yeh CT, Wang CB. Application of nickel-lanthanum composite oxide on the steam reforming of ethanol to produce hydrogen. International Journal of Hydrogen Energy 2010;35:4069–75.

[32] Siang JY, Lee CC, Wang CH, Wang WT, Deng CY, Yeh CT, et al. Hydrogen production from steam reforming of ethanol using a ceria-supported iridium catalyst: effect of different ceria supports. International Journal of Hydrogen Energy 2010;35:3456–62.

[33] Vagia EC, Lemonidou AA. Hydrogen production via steam reforming of bio-oil components over calcium aluminate supported nickel and noble metal catalysts. Applied Catalysis A: General 2008;351(1):111–21.

[34] Takanabe K, Aika K, Inazu K, Baba T, Seshan K, Lefferts L. Steam reforming of acetic acid as a biomass derived oxygenate: bifunctional pathway for hydrogen formation over Pt/ZrO2 catalysts. Journal of Catalysis 2006;243:263–9.

[35] Wu C, Sui M, Yan Y. A comparison of steam reforming of two model bio-oil fractions. Chemical Engineering & Technology 2008;31(12):1748–53.

[36] Wu C, Liu R. Carbon deposition behavior in steam reforming of bio-oil model compound for hydrogen production. International Journal of Hydrogen Energy 2010;35:7386–98.

[37] Domine ME, Iojoiu EE, Davidian T, Guilhaume N, Mirodatos C. Hydrogen production from biomass-derived oil over monolithic Pt- and Rh-based catalysts using steam reforming and sequential cracking processes. Catalysis Today 2008;133-135:565–73.

[38] Sun J. The deactivation and regeneration of industrial catalyst. Beijing, China: Press of Chemical Industry; 2006. pp. 130–136.

[39] Alenazey F, Cooper CG, Dave CB, Elnashaie SSEH, Susu AA, Adesina AA. Coke removal from deactivated Co–Ni steam reforming catalyst using different gasifying agent: an analysis of the gas-solid reaction kinetics. Catalysis Communications 2009;10:406–11.

[40] Garcia L, French R, Czernik S, Chornet E. Catalytic steam reforming of bio-oils for the production of hydrogen: effects of catalyst composition. Applied Catalysis A: General 2000; 201:225–39.

[41] Rioche C, Kulkarni S, Meunier FC, Breen JP, Burch R. Steam reforming of model compounds and fast pyrolysis bio-oil on supported nobel metal catalysts. Applied Catalysis B: Environmental 2005;61:130–9.

[42] Iojoiu E, Domine M, Davidian T, Guilhaume N, Mirodatos C. Hydrogen production by sequential cracking of biomass-derived pyrolysis oil over noble metal catalysts supported on ceria-zirconia. Applied Catalysis A: General 2007;323: 147–61.

[43] Basagiannis AC, Verykios XE. Steam reforming of the aqueous fraction of bio-oil over structured Ru/MgO/Al_2O_3 catalysts. Catalysis Today 2007;127:256–64.

[44] Medrano JA, Oliva M, Ruiz J, Garcia L, Arauzo J. Catalytic steam reforming of acetic acid in a fluidized bed reactor with oxygen addition. International Journal of Hydrogen Energy 2008;33:4387–96.